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MINERALOGICAL AND GEOCHEMICAL CHARACTERIZATION OF THE COMBUSTION WASTES ACCORDING TO THEIR INFLUENCE ON THE ENVIRONMENT

MINERALOGICKÁ A GEOCHEMICKÁ CHARAKTERIZACE ODPADŮ SPALOVÁNÍ PODLE JEJICH VLIVU NA ŽIVOTNÍ PROSTŘEDÍ

Abstract

The scope of the study is the presentation of the test results on the chemical and phase composition of combustion waste generated from several coal burning and sulphur removal technologies. The tests were run on the ash from 6 power plants which burn coal in fluid boilers and use the sulphur removal technologies involving semi-dry techniques, wet techniques and the so called clean techniques for ash from conventional boilers.

The test results indicate that the applied technology does not only have an impact on the content of basic waste components, but also differentiates their phase composition, and, accordingly, environmental impacts from the technological operations. To perform the environmental impact assessment of the ash in consideration of their disposal, the elusion test was run on the discussed waste, and next, the results compared with the limit values stipulated in relevant standards.

Abstrakt

Cílem této studie je prezentace výsledků stanovení chemického a fázového složení odpadů spalování z několika spalovacích a odsiřovacích technologií. Testy byly provedeny na popelech ze 6 elektráren, které spalují uhlí ve fluidních kotlích, a které využívají odsiřovací technologii zahrnující polo-suché, mokré a tzv. čisté technologie pro popely z konvenčních kotlů.

Key words: combustion waste, mineralogical characterization, geochemical characterization

1 INTRODUCTION

The generation of combustion wastes is an unavoidable outcome of electric energy production. Conventional waste from this process has already been well described and subjected to standardization. Upon Poland's signing the Second Sulphur Protocol aimed at reducing SO_2 emissions new coal combustion and sulphur removal technologies have been implemented in Polish power engineering. Accordingly, new types of waste have emerged. Their quality and management manners differ, depending on the applied sulphur removal method. Currently the following sulphur removal methods are used in Polish power engineering:

- Dry method of sulphur removal – involving blowing ground limestone or lime powder additives into the combustion waste. At high temperatures prevailing in the combustion chamber limestone decomposes into CaO and CO_2. Silicon dioxide binds sulphur oxide and trioxide resulting in (IV) - $CaSO_3$ sulphates and (VI) - $CaSO_4$ calcium sulphates as the main products of the sulphur removal process. The efficiency of the occurring chemical reactions depends on the size of reagent grains and on the gram-molecule ratio of calcium to sulphur. Ash containing the products of sulphur removal by means of the dry method is characterized by high content of total CaO in comparison with ash generated by means of semi-dry and fluid methods [2].

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The quantity of solid waste products ranges from 9 to 18kg/kg of the removed SO_2 [10].

- Semi-dry method of sulphur removal – involving a chemical reaction between a sorbent (often $Ca(OH)_2$) and sulfur dioxide. However, an additional phase is introduced into this reaction- a liquid one which evidently improves the efficiency of sulphur removal. Power plants utilizing this technology generate one type of combustion gas: a mixture of fly ash and: $CaSO_3 \cdot 0.5\ H_2O$, anhydrite -$CaSO_4$, calcium chloride -$CaCl_2$, sodium chloride - NaCl, calcite -$CaCO_3$, portlandite - $Ca(OH)_2$ [7]. The quantity of solid waste products ranges from 5.5 to 10 kg/kg of the removed SO_2 [10].
- Wet lime method of sulphur removal – the most effective method of sulphur removal from combustion gas. The waste is generated din the absorber as sediment, which is a mixture of sulphates IV and calcium sulphates VI. Wet methods of sulphur removal are always used after dust removal procedures and fly ash capture [4]. The final product of sulphur removal is gypsum $CaSO_4 \cdot 2H_2O$ (in the quantity of 3kg/kg of the removed SO_2), which, after dewatering, is reusable.
- Combustion in fluid chambers – enables reducing SO_2 emissions directly at source (in the boiler). The waste differs from ashes generated in combustion processes run in traditional boilers, first and foremost, due to lower temperatures of coal burning: 810 ^oC – 870 ^oC. In the course of the combustion process in a fluid chamber the liquid phase does not practically occur. Accordingly, the glassy phase is present in the ash in insignificant quantities [1, 6].

Such short review of the methods of sulphur removal from combustion gas and the types of waste generated during this process indicates that its mineralogical and chemical composition is different and, consequently, so is the impact on the environment. The usability of combustion waste for recycling depends on its chemical composition and its phase composition, which are strictly connected with the electric energy generation technology and sulphur removal technology.

The scope of the study is a mineralogical and geo-chemical characteristics of the ashes generated by Power plants using different coal burning and sulphur removal Technologies, as well as the assessment of their impact on the environment.

2 SCOPE AND METHODOLOGY OF THE RESEARCH

Eight samples of fly ash generated in different power plants and by different coal burning and sulphur removal technologies were investigated. The collected samples were prepared for the investigation in accordance with the guidelines stipulated in Standard PN-90/04502, and next subjected to chemical and phase tests.

- The tests run on the chemical composition included:
- Determination of roasting losses by means of the weight method,
- Determination of Basic chemical composition: SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, SO_3, TiO_2, P_2O_5 and of the content of selected trace elements by means of the X-ray fluorescence method,
- Leaching basic ions and trace elements from the waste.

The following determinations were made in the filtrate:

- Sulphate ions concentration by means of the weight method,
- Chloride ions concentration by means of the titration method,
- Selected trace elements concentrations by means of ICP method,
- Ph content by means of the electrometric method.

The phase composition was determined in the course of the following tests:

1. Microscopic polarization of passing and reflected light (ZEISS microscope).
2. X-rays by means of PW-1050 Philips diffractometer with copper lamp.

3 TEST RESULTS

The results confirm considerable chemical differentiation of the combustion waste (Table 1), especially as far SiO_2 and Al_2O_3 contents are concerned, but also alkaline elements of calcium oxides, sodium and potassium magnesium.

The fly ash from the sulphur removal installations utilizing the semi-dry method:

El. „R2" and El. „L2" represent, pursuant to Standard BN-79 6722-09, a calcite type (CaO > 10%), whereas the fly without the sulphur removal products from the power plants utilizing the wet methods: EC. „BB", El. „L1", El. „O" and El. „R1"- a silicate type (SiO_2 > 40%, Al_2O_3 <30). The ash from the fluid boilers, although difficult to classify due to considerable (however, not exceeding 10%) percentage of CaO may be labeled as calcite –silicate ash. The differences in the quantity of calcium content of particular components result from different operational parameters of the installations. A significant quantity of calcium in the fly ash from the sulphur removal processes is a result of using hydrated lime or limestone as sorbents of sulphur oxides; whereas, different SiO_2 content (from 45.72% to 55.08%) in the same type of the fly ash may stem from variations in the chemical composition of coal. Some specific types of combusted coal may vary in the types and quantities of mineral substances such as: silicates, calcites, sulphates and sulphides.

The content of SiO2 clearly correlates with the content of Al_2O_3. The lowest percentage of clay (16.95%) was recorded in the fly ash which had the lowest content of SiO_2.

The fly ash from sulphur removal by means of the semi-dry method has lower content of iron and magnesium in comparison with other types of ash.

High losses from the process of baking in fluid boilers especially in the case of the waste from EC. „Z" and EC. „BB". involve the presence of unburned organic substance, as proved by the follow-up microscopic tests. The quantity of the baking loss depends, to a large extend, on the accuracy of coal grinding, as well as on the combustion temperature and boiler workload. The samples collected from the fluid boilers indicate, in comparison with other waste samples, the highest SO_3 content, resulting from the presence of anhydrite ($CaSO_4$), which is a product of combustion waste sulphur removal, as certified by X-ray and microscopic tests. In the tested waste, the Na_2O content is within the range of 0.55% - 1.18%, whereas, K_2O from 1.65% to 3.07%. On the grounds of the quantitative analysis it is impossible to say whether they constitute the amorphous phase or whether they are related to thermally untransformed illite phase.

The results of the determinations of selected trace elements such as: As, Ba, Cd, Cr, Cu, Ni, Pb, and Zn indicate considerable fluctuations in their concentration in the fly ash, especially as far as Ni and Cr are concerned (Table 2). The concentrations of the determined heavy metals still comply with the values quoted in available professional literature [5, 11]. The quantity of a given element in the burnt coal has a big influence on the concentration of metals in the combustion waste. Also, a lot depends on the combustion process conditions, for example, on the temperature prevailing in the chamber, as well as on the coal grain size distribution.

In the tested combustion waste Cd was practically undetected. In the course of coal combustion in oxygen environment at high temperatures this element changes into (passes over to) gas-like compounds , yet a part of it may condense on the fly ash particles, which could be the case of the fly ash from EL. „L2" [12].

Table 1 Chemical composition of the investigated waste

Determination types [mg/dm^3]	Fluidized bed ash EC. Z	Fluidized bed ash EC. BP	Fly ash EC. BB	Fly ash EL. L1	Fly ash EL. O	Fly ash EL. R1	Fly ash and semi-dry sulphur removal by products EL. R2	Fly ash and semi-dry sulphur removal by products EL. L2
Sulphate SO_4^{2-}	1503.6	1230.3	179.9	263.8	249.8	192.2	1274.3	303.3
Chloride Cl^-	118.8	192.2	12.38	5.5	4.2	10.66	610.7	341.1
As	n.o	<0.05	<0.05	<0.05	n.o	<0.05	<0.05	<0.05
Cr	0.02	<0.02	0.04	0.12	0.11	0.26	0.15	0.1
Cu	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Fe	<0.02	0.07	0.07	<0.02	<0.02	0.08	0.05	<0.02
Ni	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Pb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Zn	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
pH	>12	11.24	11.76	11.59	>12	>12	>12	>12

Table 2 Selected toxic elements content in the investigated waste

Toxic element [ppm]	Fluidized bed ash EC. Z	Fluidized bed ash EC. BP	Fly ash EC. BB	Fly ash EL. L1	Fly ash EL. O	Fly ash EL. R1	Fly ash and semi-dry sulphur removal by products EL. R2	Fly ash and semi-dry sulphur removal by products EL. L2
As	n.o	18	28	n.o	15	14	10	18
Ba	1784	631	1237	1054	1795	1478	1250	896
Cd	n.o	n.o	n.o	n.o	n.o	n.o	n.o	17
Cr	69	28	85	189	142	98	52	127
Cu	69	8	n.o	107	43	31	27	82
Ni	38	n.o	48	95	53	92	16	77
Pb	238	132	76	128	138	124	132	156
Zn	168	250	173	224	251	358	260	256

Table 3 Elution of basic ions and trace elements in the tested combustion waste

Determination types [mg/dm^3]	Fluidized bed ash EC. Z	Fluidized bed ash EC. BP	Fly ash C. BB	Fly ash EL. L1	Fly ash EL. O	Fly ash EL. R1	Fly ash and semi-dry sulphur removal by products EL. R2	Fly ash and semi-dry sulphur removal by products EL. L2
Sulphate SO_4^{2-}	1503.6	1230.3	179.9	263.8	249.8	192.2	1274.3	303.3
Chloride Cl^-	118.8	192.2	12.38	5.5	4.2	10.66	610.7	341.1
As	n.o	<0.05	<0.05	<0.05	n.o	<0.05	<0.05	<0.05
Cr	0.02	<0.02	0.04	0.12	0.11	0.26	0.15	0.1
Cu	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Fe	<0.02	0.07	0.07	<0.02	<0.02	0.08	0.05	<0.02
Ni	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Pb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Zn	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
pH	>12	11.24	11.76	11.59	>12	>12	>12	>12

One of the methods of assessing the negative impact of waste is the analysis of the water extract obtained in the leaching test.

The chemical analyses of the extracts of the tested waste show that the fluid ash (EC. „Z" and EC. „BP"), as well as the ash containing sulphur removal products (El. „R2") clearly point to bigger concentration of sulphate ions (Table 3), due to the combustion process in fluid boilers. The addition of a sorbent results in the transformation of sulphur dioxide $CaSO_4$, the ions of which are easily soluble in water. Such high mineral content of the tested water extracts is also caused by chloride ions, which leached from the ashes containing the sulphur removal products of El. „R2". Their presence is an outcome of a simultaneously occurring reaction of chlorine ions binding, leading to the formation of $CaCl_2$.

The water extracts of all tested fly ash also indicate higher pH values, yet still within the average range determined for combustion waste. The alkaline reaction of the extracts undoubtedly exerts a positive impact on the immobility of heavy metals, which were not detected in the elutions at the assumed determination level of the method. Trace contents of heavy metals in the extracts indicate that, in consideration of such high pH value of the solution, they make up insoluble or slowly-soluble forms. Probably, these metals do not constitute independent minerals but are parts of glaze or a diadochid admixture in other minerals.

The determination of the phase composition of the tested waste was mainly based on the X-ray analysis (Table 4) and microscopic analysis (Photographs: 1-18).

The same phase detected in all the tested waste is quartz, most commonly occurring in sharp-edge grains (Photograph 10), or possibly, included grains in cryptocrystalline aggregates. In view of small dimensions, the identification of this component is often difficult.

Another phase observed in all of the tested fly ash involves magnetite and hematite due to the oxidation of pyrite.

In the course of microscopic observations it was observed that magnetite is a common component of spherical aggregates, where it usually makes up spherical forms of well preserved skeleton structure (Photograph 4). The external surface of the spherical aggregates is often subjected to the process of hematite oxidation- martitising (Photograph 5).

Hematite is found in considerably smaller quantities than magnetite. In the passing light it is transparent with a slight red-like colour. In the reflected light it differs from magnetite because of its brighter colour and clearer anisotropy.

Table 4 The results of the X-ray analysis of the investigated wastes

Mineral / Sample	Quartz	Mullite	Calcite	Anhydrite	Hannebachite	Portlandite	Bassanite	Merwinite	Hydrophilite	Periclase	Magnetite	Hematite	Maghemite	Albite
1. EC. „Z"	+			+			+		+	+		+	+	+
2. EC. „BP"	+			+			+	+	+	+		+	+	+
3. EC. „BB"	+	+									+	+		+
4. EL. „L1"	+	+					+			+	+	+	+	+
5. EL. „O"	+	+									+	+		+
6. EL. „R1"	+	+									+	+		+
7. El. „R2"	+	+	+	+	+		+	+			+	+		
8. EL. „L2"	+	+	+		+	+					+	+		

Often badly-polished grains have blood-like internal reflections, masking their interference colours (Photograph 4). In the samples of the fly ash from El. „L1" not containing the sulphur removal products metallic iron of spherical shape and grain size about 100 µm was sporadically observed, of white colour (brighter than magnetite and hematite), and of isotropic nature (Photograph 3). One of the main components present in the fly ash from the tested fluid boilers was anhydrite, often making up conglomerates (Photograph 7), although idiomorphic grains were also found (Photograph 8). The ash from the fluid boilers and sulphur removal by means of the semi-dry method contained gypsum/ bassanite. Unfortunately, on the grounds of the X-ray tests it is impossible to conclude if this is primal gypsum (which did not enter the high temperature zone) or the outcome of lime synthesis from the decomposition of carbonates in the course of the combustion process.

The ash generated at higher temperatures, i.e. in conventional boilers contain mullite (Photograph 9), which is the end product of thermally transformed clay mineral substance contained in the input coal. The presence of active puzzolan phase in the form of dehydrated clay minerals of high specific surface enhances the quality of this ash as modifiers of cement binders [8].

The amorphous phase of the tested ash is mainly represented by spherical aggregates of various colours. Glassy blank spherical grains may be classified as melitite or gehlenite. Glassy yellowish colour is probably $CaO\text{-}Fe_2O_3\text{-}SiO_2$ (Photograph 11).

A considerable part of the fly ash from the fluid boiler of EC. „Z", are porous fragments of unburned coal (Photograph 1.2). These grains are often characterised by oval shape pores, separated by unburned organic substance (Photograph 1), often called: "laces" or "tablecloths" in professional literature [9]. The ashes containing a lot of unburned organic matter have higher water demand due to water absorption to the inside of porous coking coal grains.

4 CONCLUSIONS

The tests conducted on fly ash from several power plants indicated considerable difference in the generated waste, both in its chemical composition and phase composition.

- The biggest variations in the chemical composition (especially in SiO_2 and Al_2O_3 content) were detected in the ash from fluid boilers. Due to high content of CaO, yet not exceeding 10%, the tested ash should be classified as silicate and calcite ash. The ash from the „R2" Power Plant and „L2" Power Plant that make use of semi-dry sulphur removal techniques represent the calcite type. In view of a high content of CaO they should be classified as active waste. „Clean" ashes that does not contain sulphur removal by-products from the „BB" Heat and Power Generation Plant, the „L1", „R1", and „O" Plant, despite variations in silicon dioxide content from 45.72% to 55.08%, represent, in accordance with the binding standards, the silicate type. High content of silicon dioxide in this waste with the simultaneous low CaO percentage, lead to the conclusion that his ash has low chemical activity.
- The most environmentally hazardous ash, in view of their eventual disposal, is the ash that does not contain sulphur removal Bi-products. A decisive impact on the process of mineralizing external waters migrating through fluid waste and fly ash generated in the course of applying sulphur removal technologies by means of semi-dry techniques comes from sulphur ions and chloride ions. The concentration of SO_4^{2-} which is 7 times higher than the one in the water extract from the waste in comparison with „clean" ash in as outcome of the sulphur removal process.
- Low content of heavy metals in water elution indicate that most probably, with such high water pH, metal positive ions make up forms that are indissoluble or slow-soluble in the eluate and are only present in trace elements. It should be remembered; however, that some components may be actuated only in specific conditions or after a certain passage of time. After long-term deposition, the discussed waste may lose its alkali properties and lead to selective leaching of heavy metals to the environment [3].
- X-ray tests and microscope examinations of particular ash indicated different qualitative and quantitative compositions of the identified materials. In view of the quantitative relations between the specific elements of some particular phase elements, it should be possible to control the properties of the materials derived in further utilization of their ash.

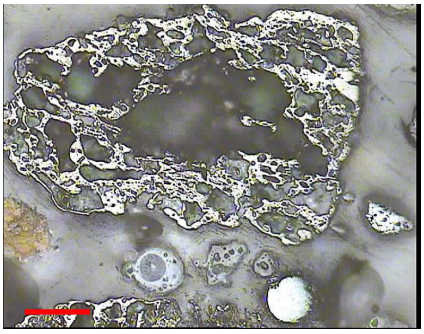

Fig.1: Organic matter. Fly ash sample from the „L" Power Plant Reflected light, 1N, magn. 100x

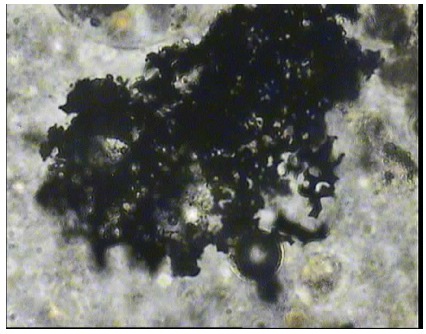

Fig.2: Organic matter. Fluidized bed ash from the "Z" Power Plant. Transmission microscopy, 1N, magn. 200x.

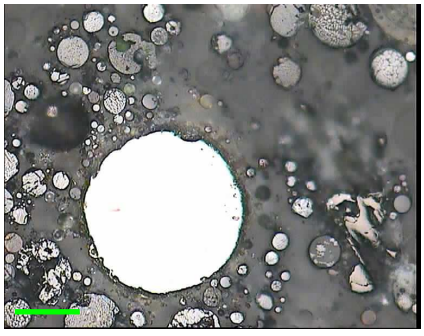

Fig.3: Metallic iron. Fly ash sample from the "L" Power Plant. Reflected light, 1N magn. 200x.

Fig.4: Magnetite with hematite. aureole. Fluidized bed ash sample from the "BP" Power Plant. Reflected light, NX, magn.

Fig.5: Magnetite with hematite aureole. Fly ash sample from the "L" Power Plant. Reflected light, 1N, magn. 500x.

Fig.6: Skeletal structure of magnetite. Fly ash sample from the "L" Power Plant. Reflected light, 1N, magn. 500x.

Fig.7: Anhydrite conglomerate. Fluidized bed ash sample from the "BP" Power Plant. Reflected light, 1N magn.

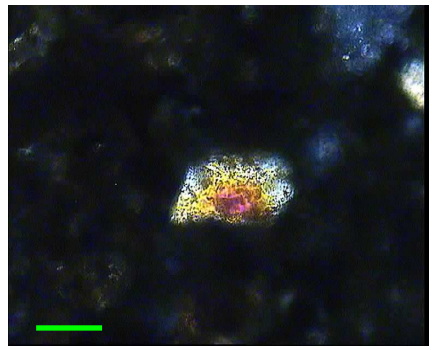

Fig.8: Anhydrite. Fluidized bed ash sample from the "BP" Power Plant. Transmission microscopy, NX magn. 200x.

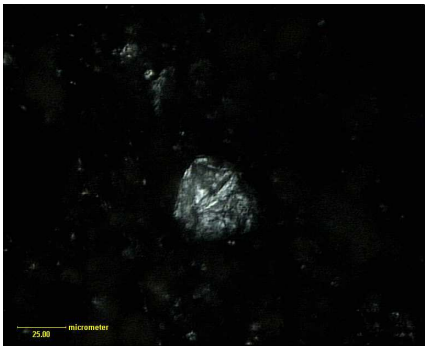

Fig.9: Mullite conglomerate. Fly ash sample from the "R" Power Plant. Transmission microscopy, NX,

Fig.10: Quartz. Fly ash sample from the "R" Power Plant. Transmission microscopy, NX, magn. 400x.

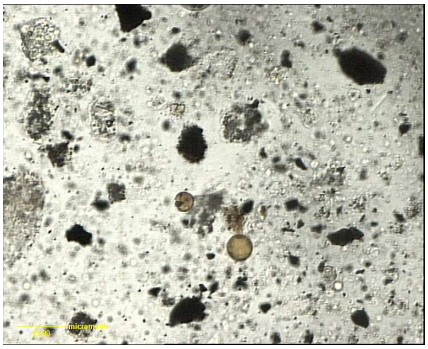

Fig.11: Glaze with different colours. Fly ash sample from the "R" Power Plant. Transmission microscopy, 1N magn. 100x.

Fig.12: Cenospheres. Fly ash sample from the "L" Power Plant. Reflected light, 1N, magn. 200x.

REFERENCES

[1] BABOLEWSKI, P. & KANAFEK, J.: Praktyczne zastosowanie popiołów dennych z kotłów fluidalnych jako regulator wiązania cementu. X Jubileuszowa Międzynarodowa Konferencja – Popioły z Energetyki. Warszawa 14-17 X 2003.

[2] DROBEK, L.: Ocena chemizmu odpadów energetycznych w podziemnych wyrobiskach górniczych. X Jubileuszowa Międzynarodowa Konferencja – Popioły z Energetyki. Warszawa 14-17 X 2003.

[3] CHODYNIECKA, L.,: Wpływ zwałowisk odpadów hutniczych na środowisko Górnego Śląska. Zeszyty Naukowe Politechniki Śląskiej. Górnictwo zeszyt 256, Gliwice, 2003

[4] CHUDEK, M., JANICZEK, S. & PLEWA, F.: Materiały w budownictwie geotechnicznym tom1. Materiały w budownictwie podziemnym. Wydawnictwo Politechniki Śląskiej Gliwice, 2001

[5] HANAK, B. & KOKOWSKA-PAWŁOWSKA, M.: Zróżnicowanie zawartości pierwiastków śladowych i podrzędnych w skałach płonnych i popiołach węgla z pokładu 620. Zeszyty Naukowe Politechniki Śląskiej. Seria: Górnictwo 2004.

[6] KABAŁA, J. i in. Własności i zastosowanie ubocznych produktów spalania węgla w kotłach fluidalnych. Popioły z energetyki. Monografia, Kraków 6-8 listopada 2006.

[7] KUCOWSKI, J., LAUDYN, D. & PRZEKWAS, M. : Energetyka a ochrona środowiska. Wydawnictwa Naukowo-Techniczne. Warszawa 1997.

[8] MAŁOLEPSZY, J. & PYTEL, Z.: Effekt of Metakaolinite on Strength Chemical Resistance of Cement Mortars", V International Conference on Durability of Concrete CANMET/ ACI, Barcelona 2003.

[9] MISZ, M., DONIECKI, T. & CEBULAK, S.: Charakterystyka popiołów lotnych i popiołów dennych z kotła fluidalnego działającego w elektrowni Jaworzno II. Zeszyty Naukowe Politechniki Śląskiej. Seria Górnictwo z.268, Gliwice 2005.

[10] PACHOWSKI, J.: Rozwój technologii powstawania ubocznych produktów elektrownianych oraz ich charakterystyka i możliwości zastosowań w technologiach budownictwa drogowego. Drogi i mosty, nr 1, 2002.

[11] STAISZ, J., PASOŃ-KONIECZYŃSKA, A. & KONIECZYŃSKI, J.: Bilans pierwiastków śladowych emitowanych w procesie spalania węgla kamiennego. Politechnika Śląska, 1999.

[12] YUDOVICH, Ya.E. & KETRIS, M.P.: Russian Academie of sciences. Institut of Geology. Toxic Trace Elements in coal, Ekaterinburg, 2005.

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